

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-330855

(43)Date of publication of application : 15.12.1998

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(51)Int.Cl.

C22B 7/00  
B09B 5/00

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(21)Application number : 09-159194

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(22)Date of filing : 02.06.1997

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## (54) METHOD FOR RECOVERING VALUABLE MATERIAL FROM LITHIUM-ION SECONDARY BATTERY

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To easily recover the valuable material from an exterior material high yield by charging the defective product and the used product at of a lithium ion secondary battery into a rotary kiln held at a specific temp. and rupturing and separating the contents.

**SOLUTION:** The defective product developed in a manufacturing process of the lithium secondary battery and the used battery are charged into the rotary kiln heated at  $\geq 800^{\circ}\text{C}$ , and the contents in the battery are ruptured at the high temp., and the valuable materials containing Co in the battery are spouted from the iron-made exterior material and burnt. The burnt powder of this valuable materials is recovered by a method of gravity precipitation, cyclone, bag filter, etc., and also, the contents of metal-made exterior material, copper film, etc., are separately recovered. Since only the contents of the valuable material are ruptured without rupturing the exterior material while maintaining the original shape, and separated from the exterior material, the valuable material of Co, etc., and be recovered at high yield.

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## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

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[Claim(s)]

[Claim 1] The recovery approach of the valuables from the rechargeable lithium-ion battery characterized by throwing a rechargeable lithium-ion battery into the furnace heated at 800 degrees C or more, bursting a cell, and separating valuables powder from a sheathing material [claim 2] The approach according to claim 1 a furnace is rotary kiln

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the approach of collecting valuables, for example, cobalt, from a rechargeable lithium-ion battery.

[0002]

[Description of the Prior Art] A rechargeable lithium-ion battery is small and lightweight, are high electric capacity and a high voltage, and is extensively used focusing on portable electronic equipment, such as a notebook personal computer, a cellular phone, and a digital camera. By this cell, the ingredient of the carbon system the multiple oxide of the cobalt whose positive electrode is a valuable metal as an active material, and a lithium is applied to aluminium foil, and a negative electrode's is [ system ] an active material at copper foil is applied. Moreover, iron is used for the can-like Lord as a cell sheathing material. Thus, valuables, such as cobalt, are contained in the rechargeable lithium-ion battery.

[0003] On the other hand, a defective generates this cell in a manufacture process. Moreover, this cell is used extensively as mentioned above, and will be discarded in connection with the life of a use device and a cell. It is very more important than the viewpoint of a deployment of a resource to collect valuables, such as cobalt, efficiently and cheaply from a used cell in the defective list in these production processes. Conventionally, the approach of sifting out is proposed as a core after combustion and crushing as an approach of collecting the valuables from a used rechargeable lithium-ion battery (JP,6-346101,A). However, since the electrode material is [ the sheathing material ] comparatively thick a precise roll, a burned rechargeable lithium-ion battery is difficulty debris. Therefore, even if crushing is possible, crushing effectiveness is very bad, and debris cannot sift out easily the valuables which will be in the condition that it was involved in by the sheathing material, and contain cobalt with sufficient recovery.

[0004]

[Problem(s) to be Solved by the Invention] It is offering the approach of collecting valuables, such as cobalt, from a rechargeable lithium-ion battery efficiently.

[0005]

[Means for Solving the Problem] That is, this invention is the recovery approach \*\*\*\* of the valuables from the rechargeable lithium-ion battery characterized by throwing a rechargeable lithium-ion battery into the furnace heated at 800 degrees C or more, bursting a cell, and separating valuables powder from a sheathing material. Furthermore, in order to carry out this invention industrially, rotary kiln can use it the optimal.

[0006]

[Embodiment of the Invention] The rechargeable lithium-ion battery consists of a sheathing material of a cell, and contents [a positive electrode, a negative electrode, and an electrolyte (electrolytic solution)] of a cell, and contains an organic substance as a component of the electrolytic solution. That is, an organic substance is polyvinylidene fluoride which is the binder of an active material at electrolytes, such as a 6 phosphorus-fluoride acid lithium which is dissolving in organic solvents, such as propylene carbonate which is the electrolytic solution, and the electrolytic solution, the porosity polypropylene used for inter-electrode as an insulator thin film, and a list. Especially, with the flash point around 100 degrees C, an organic solvent is a flammability and is contained about 10 to 20% of the weight in the cell.

[0007] In this invention, a rechargeable lithium-ion battery is directly switched on in a hot furnace 800 degrees C or more. Since the temperature rise of the cell is rapidly carried out in that case, the combustible in the contents of a cell burns explosively, and a cell can explode and can separate the valuables in the contents of a sheathing material and a cell efficiently. Usually, the sheathing material of a cell is cylindrical [ which has telescopic / metal /, for example, a bottom, ], and has structure which put the roll-like cell

structure into the interior and put the top cover, and a top cover is \*\*\*\*\* with a caulking to a cylinder. It is that the organic substance whose bursts are the contents of a cell rapidly when a cell is placed into a hot furnace expands, a top cover falls out, the cell structures, such as copper foil, escape from a sheathing object, come out, and burn further, and valuables powder is generated. Although the pinhole of gas drainage is prepared in the sheathing material, when usually being based on rapid heating, this pinhole is insufficient for a cell and a burst takes place to it.

[0008] In order to burst a cell, the temperature of the combustion furnace which switches on a cell is 800 degrees C or more, and is 1000 degrees C or more more preferably 900 degrees C or more. It becomes impossible to burst 90% or more of cell, and it becomes impossible to do the purpose of this invention so at less than 800 degrees C. If a cell explodes, the contents included by the sheathing material will blow, and will come out and burn, and valuables powder will be made. Processing of the valuables powder which came out of the sheathing material can adopt various well-known approaches. For example, the powder component which is fines originally in order that an organic component may disappear by combustion can be put on combustion gas, and can be easily taken out outside a combustion furnace. The valuables powder in combustion gas is recoverable by well-known approaches, such as gravitational settling, a cyclone, and a bag filter. Moreover, a scrubbing tower can be used and it can collect also with wet. Moreover, the valuables powder which does not become fines crushes still more nearly additionally the sheathing material which could also dissociate by sieving etc. if needed and exploded on the screen lot, and it may be sifted out after that and it may separate it.

[0009] The combustion furnace used for operation of this invention is employable with the combustion furnace of any formats, if sufficient air required for combustion and recovery of valuables powder can be supplied and discharged. However, the rotary kiln with easy inflow of air and discharge which can be processed continuation extensive is desirable. Although the powder of valuables rides on combustion gas and comes outside a firing furnace in order that the contents of the cell by which the cell sheathing material and contents which exploded by rotation of a rotary kiln rotate the inside of a rotary kiln, and contain valuables powder may come out of a cell completely, when based on a rotary kiln, separation recovery of the metals, such as copper foil which is an electrode material, and iron which is a cell sheathing material, is discharged and carried out more nearly separately than a firing furnace.

[0010] Although valuables are matter for which recovery included in the contents, for example, a negative electrode, held by the cell sheathing material, a positive electrode, and the electrolytic solution is targeted and it changes variously with classes of cell, there are manganese, a lithium, vanadium, nickel, cobalt, etc. The crushing process was [ after burning a cell ] indispensable in order to collect valuables from a rechargeable lithium-ion battery. However, since a calcinated rechargeable lithium-ion battery was difficulty debris, effectiveness worsened very much, but passing through a crushing process can collect valuables efficiently, without passing through a crushing process, if the approach by this invention is adopted.

[0011]

[Example] Next, although an example is given and this invention is explained concretely, this does not limit this invention at all.

[0012] When the small furnace with example 1 volume of about 4.5l. (15cmx10cmx30cm) was held at 850 degrees C and 3 (total weight of 118.2g) injections of the cylindrical rechargeable lithium-ion battery (the diameter of 18mm, die length of 65mm, weight of 39.4g) were carried out, it exploded and burned with the explosion after several seconds. The top cover of all cells separated and it was divided into a sheathing material and cell contents (copper foil and valuables powder). The sheathing material was maintaining the configuration before baking by a cylinder and a top cover without a top cover, and total weight was 25.5g. Cell contents became 11.1g of roll-like copper foil, and 55.5g of black valuables powder, and valuables powder contained cobalt 37.5% by 60 or less meshes.

[0013] Although the same small furnace as example of comparison 1 example 1 was held at 700 degrees C, and three rechargeable lithium-ion batteries (the diameter of 18mm, die length of 65mm) were switched on and burned, one carried out burst combustion, and other two had burned, with the gestalt maintained.

[0014] Beforehand, the kerosene burner was burned, the temperature up of the rotary kiln with an example 2 die length [ of 8000cm ] and a diameter of 500cm was carried out to 900 degrees C, and the sequential injection of the used rechargeable lithium-ion battery was carried out. Since a cell was rapidly exposed to an elevated temperature, combustibles, such as an organic solvent in a cell, burned rapidly, it exploded, and the valuables powder containing cobalt blew off in combustion gas. In order to carry out self-sustained combustion of the cell, finally the temperature of kiln maintained temperature at about 1050 degrees C only by combustion of a cell completely, having gone up and extracting a kerosene burner, and continued the

injection of a cell. In this rotary kiln, 1050 degrees C was maintained by carrying out the 150 kg/hr injection of the cell, and the combustion accompanied by the burst of a cell was continued.

[0015] 97.5% of the cell (weight) exploded. The valuables powder in which the exhaust gas discharged from the kiln containing valuables powder contains cobalt with each powder uptake equipment via a gravity settling tank, a cyclone, and a bag filter was collected. It burned in 850kg of cells, and 468kg of 178kg of sheathing materials and cell contents (copper foil and valuables powder) which burned were obtained. The sheathing material was maintaining the configuration before baking mostly, although there were also a cylinder without a top cover and a thing which transformed some by the top cover. Cell contents are 78kg of copper foil, and 390kg of valuables powder, and valuables powder contained cobalt 38.3% by 60 or less meshes.

[0016]

[Effect of the Invention] As for the rechargeable lithium-ion battery, valuables, such as copper including cobalt and iron, are contained. Without crushing a cell substantially according to this invention, the valuables in the contents of a cell can be separated from a sheathing material, and expensive valuables, such as cobalt, can be efficiently collected by low cost.

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[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11) 特許出願公開番号

特開平10-330855

(43) 公開日 平成10年(1998)12月15日

(51) Int.Cl.<sup>8</sup>

識別記号

F I

C 2 2 B 7/00

C 2 2 B 7/00

C

B 0 9 B 5/00

Z A B

B 0 9 B 5/00

Z A B A

審査請求 未請求 請求項の数 2 F D (全 3 頁)

(21) 出願番号 特願平9-159194

(22) 出願日 平成9年(1997)6月2日

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(54) 【発明の名称】 リチウムイオン二次電池からの有価物の回収方法

(57) 【要約】

【課題】リチウムイオン二次電池から外装材の内部の有価物を効率的に回収する方法を提供することである。

【解決手段】リチウムイオン二次電池を、800℃以上に加熱された炉に投入し、電池を破裂させコバルトを含む有価物を粉末状で分離回収する。

## 【特許請求の範囲】

【請求項1】リチウムイオン二次電池を、800℃以上に加熱した炉に投入し、電池を破裂させ、外装材から有価物粉末を分離することを特徴とするリチウムイオン二次電池からの有価物の回収方法

【請求項2】炉がロータリーキルンである請求項1記載の方法

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、リチウムイオン二次電池から有価物例えばコバルトを回収する方法に関する。

## 【0002】

【従来の技術】リチウムイオン二次電池は、小型、軽量で高電気容量かつ高電圧であり、ノートブックパソコン、携帯電話、デジタルカメラ等の携帯用の電子機器を中心に広範に利用されている。本電池では、正極は、例えば活物質として有価金属であるコバルトとリチウムの複合酸化物がアルミニウム箔に塗布されており、負極は銅箔に活物質である炭素系の材料が塗布されている。また、電池外装材として缶状の主に鉄が使用されている。このように、リチウムイオン二次電池にはコバルト等の有価物が含まれている。

【0003】一方、本電池は製造過程で不良品が発生する。また、本電池は上述のように広範に使用されており、使用機器および電池の寿命に伴い廃棄されることになる。これらの製造工程での不良品並びに使用済電池よりコバルト等の有価物を効率的かつ安価に回収することは資源の有効利用の観点より非常に重要である。従来、使用済みリチウムイオン二次電池からの有価物を回収する方法として、燃焼、破碎後、篩分けする方法を中心として提案されている（特開平6-346101）。しかしながら、燃焼済みリチウムイオン二次電池は外装材が比較的厚く、且つ電極材料が緻密な巻物になっているため難破碎物である。そのため、破碎ができたとしても非常に破碎効率が悪く、また、破碎物は外装材で巻き込まれたような状態となりコバルトを含む有価物を、容易に回収率良く篩分けすることができない。

## 【0004】

【発明が解決しようとする課題】リチウムイオン二次電池からコバルト等の有価物を効率的に回収する方法を提供することである。

## 【0005】

【課題を解決するための手段】すなわち、本発明は、リチウムイオン二次電池を、800℃以上に加熱した炉に投入し、電池を破裂させ、外装材から有価物粉末を分離することを特徴とするリチウムイオン二次電池からの有価物の回収方法ある。更に、本発明を工業的に実施するには、ロータリーキルンが最適に使用できる。

## 【0006】

【発明の実施の形態】リチウムイオン二次電池は、電池の外装材と電池の内容物〔正極、負極及び電解質（電解液）〕からなっており、電解液の成分として有機物質を含む。すなわち、有機物質は電解液であるプロピレンカーボネート等の有機溶剤、電解液に溶解している六フッ化リン酸リチウム等の電解質、電極間に絶縁体薄膜として用いる多孔質ポリプロピレン、並びに、活物質の結着剤であるポリフッ化ビニリデン等である。特に、有機溶剤は100℃前後の引火点を持ち可燃性であり、電池中に10～20重量%程度含まれている。

【0007】本発明においては、リチウムイオン二次電池を800℃以上の高温の炉内に直接投入する。その際、電池は急激に温度上昇するため、電池の内容物中の可燃物は爆発的に燃焼し電池は破裂し、外装材と電池の内容物中の有価物を効率的に分離することができる。通常、電池の外装材は、金属製の筒型例えば底のある円筒型等であり、内部に巻物状の電池構造体を入れ上蓋を被せた構造となっており、上蓋は円筒にかしめ付てある。破裂とは、電池が高温の炉内に置かれると急激に電池の内容物である有機物質が膨張し上蓋が抜け更に銅箔等の電池構造体が外装体から抜け出て燃焼し、有価物粉末が生成されることである。電池には、通常、ガス抜き的小穴が外装材に設けられているが急激な加熱による場合はこの小穴では不十分であり破裂が起こる。

【0008】電池を破裂させるためには、電池を投入する燃焼炉の温度は800℃以上であり、好ましくは900℃以上、より好ましくは1000℃以上である。800℃未満では、90%以上の電池を破裂させることができなくなり、本発明の目的を奏することができなくなる。電池が破裂すると、外装材で包含された内容物が吹き出て燃焼し、有価物粉末ができる。外装材の外に出た有価物粉末の処理は、種々の公知の方法が採用できる。例えば、燃焼により有機成分が消失するため元来微粉である粉末成分を、燃焼ガスに乗せて燃焼炉外に容易に取り出すことができる。燃焼ガス中の有価物粉末は、重力沈降、サイクロン、バグフィルター等の公知の方法により回収できる。また、洗浄塔を利用し湿式にても回収が可能である。又、微粉にならない有価物粉末は、必要に応じて篩分け等により分離することもでき、又、篩分け前に破裂した外装材を更に付加的に破碎して、その後篩分けして分離してもよい。

【0009】本発明の実施に用いる燃焼炉は、燃焼および有価物粉末の回収に必要な十分の空気を供給し、かつ排出できるものであればいかなる形式の燃焼炉でも採用が可能である。ただし、連続大量処理が可能で、かつ空気の流入、排出が容易であるロータリーキルンが好ましい。ロータリーキルンによる場合、ロータリーキルンの回転により破裂した電池外装材及び内容物がロータリーキルン内を回動し有価物粉末を含む電池の内容物は、完全に電池から出るため、有価物の粉末は燃焼ガスに乗って焼成

炉外に出るが、電極材料である銅箔、電池外装材である鉄等の金属は、別途焼成炉より排出され、分離回収される。

【0010】有価物とは、電池外装材で保持された内容物例えば負極、正極及び電解液に含まれる回収を目的とされる物質であり、電池の種類により種々異なるが、マンガ、リチウム、バナジウム、ニッケル、コバルトなどがある。リチウムイオン二次電池から有価物を回収するためには、電池を燃焼後、破碎工程が必須であった。しかしながら、破碎工程を経ることは、焼成済みリチウムイオン二次電池が、難破碎物であるため、非常に効率が悪くなったが、本発明による方法を採用すると破碎工程を経ずに効率的に有価物を回収することができる。

【0011】

【実施例】次に、実施例を挙げて本発明を具体的に説明するが、これにより、本発明を何ら限定するものではない。

【0012】実施例1

容積約4.5リットル(15cm×10cm×30cm)の小型炉を850℃に保持し、円筒型リチウムイオン二次電池(直径18mm、長さ65mm、重量39.4g)を3本(全重量118.2g)投入したところ、数秒後に爆発音と共に破裂し燃焼した。すべての電池の上蓋が外れ、外装材と電池内容物(銅箔及び有価物粉末)に分かれていた。外装材は、上蓋のない円筒と上蓋で焼成前の形状を維持しており、全重量は25.5gであった。電池内容物は、巻物状の銅箔11.1gと黒色の有価物粉末55.5gになり、有価物粉末は60メッシュ以下でコバルトを37.5%含んでいた。

【0013】比較例1

実施例1と同一の小型炉を700℃に保持しリチウムイオン二次電池(直径18mm、長さ65mm)を3本投

入し燃焼させたが、1本のみ破裂燃焼し、他の2本は形態を保ったまま燃焼していた。

【0014】実施例2

長さ8000cm、直径500cmのロータリーキルンを、あらかじめ、灯油バーナーを燃焼させ、900℃に昇温し、使用済みリチウムイオン二次電池を順次投入した。電池は急激に高温にさらされるため電池中の有機溶剤等の可燃物が急激に燃焼、破裂し、コバルトを含む有価物粉末が燃焼ガス中に吹き出した。電池は自燃するためキルンの温度は上昇し、灯油バーナーを絞りながら最終的には完全に電池の燃焼のみで1050℃程度に温度を維持し、電池の投入を継続した。このロータリーキルンでは電池を150Kg/h投入することで1050℃を維持し電池の破裂を伴う燃焼は継続した。

【0015】電池の97.5%(重量)が破裂した。有価物粉末を含むキルンより排出される排ガスは、重力沈降槽、サイクロン、バグフィルターを経由し、それぞれの粉末捕集装置にて、コバルトを含む有価物粉末が回収された。電池850Kgを燃焼し、燃焼した外装材178Kgと電池内容物(銅箔と有価物粉末)を468Kg得た。外装材は、上蓋のない円筒と上蓋で多少変形したものもあるが焼成前の形状をほぼ維持していた。電池内容物は、銅箔78Kgと有価物粉末390Kgであり、有価物粉末は、60メッシュ以下でコバルトを38.3%含んでいた。

【0016】

【発明の効果】リチウムイオン二次電池はコバルトをはじめとして銅、鉄等の有価物が含まれている。本発明によると実質的に電池を破碎することなく、電池の内容物中の有価物を外装材から分離することができ、コバルト等の高価な有価物を効率的に低コストで回収することができる。